

Environmental Protection Agency

Pt. 136, App. A, Meth. 603

METHOD 603—ACROLEIN AND ACRYLONITRILE

1. Scope and Application

1.1 This method covers the determination of acrolein and acrylonitrile. The following parameters may be determined by this method:

| Parameter | STORET No. | CAS No. |
|---------------------|------------|----------|
| Acrolein | 34210 | 107-02-8 |
| Acrylonitrile | 34215 | 107-13-1 |

1.2 This is a purge and trap gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for either or both of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for the parameters listed above, if used with the purge and trap conditions described in this method.

1.3 The method detection limit (MDL, defined in Section 12.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the analytes are trapped. After the purge is completed, the trap is heated and backflushed with the inert gas to desorb the compound onto a gas chromatographic column. The gas chromatograph is temperature programmed to

separate the analytes which are then detected with a flame ionization detector.^{2,3}

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compound outgassing from the plumbing of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high analyte levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105°C between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this view point, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{4,6} for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: a purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device must be capable of being heated to 85 °C within 3.0 min after transfer of the sample to the purging device and being held at 85 ± 2 °C during the purge cycle. The entire water column in the purging device must be heated. Design of this modification to the standard purging device is optional, however, use of a water bath is suggested.

5.2.1.1 Heating mantle—To be used to heat water bath.

5.2.1.2 Temperature controller—Equipped with thermocouple/sensor to accurately control water bath temperature to ± 2 °C. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain 1.0 cm of methyl silicone coated packing (Section 6.5.2) and 23 cm of 2,6-diphenylene oxide polymer (Section 6.5.1). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber must be capable of rapidly heating the trap to 180 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit as illustrated in Figure 3 or be coupled to a gas chromatograph.

5.3 pH paper—Narrow pH range, about 3.5 to 5.5 (Fisher Scientific Short Range Alkacid No. 2, #14-837-2 or equivalent).

5.4 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required acces-

sories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.4.1 Column 1—10 ft long x 2 mm ID glass or stainless steel, packed with Porapak-QS (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.4.2 Column 2—6 ft long x 0.1 in. ID glass or stainless steel, packed with Chromosorb 101 (60/80 mesh) or equivalent.

5.4.3 Detector—Flame ionization detector. This type of detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.5 Syringes—5-mL, glass hypodermic with Luerlok tip (two each).

5.6 Micro syringes—25-μL, 0.006 in. ID needle.

5.7 Syringe valve—2-way, with Luer ends (three each).

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrisorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.4 Hydrochloric acid (1+1)—Slowly, add 50 mL of concentrated HCl (ACS) to 50 mL of reagent water.

6.5 Trap Materials:

6.5.1 2,6-Diphenylene oxide polymer—Tenax (60/80 mesh), chromatographic grade or equivalent.

6.5.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in reagent water using assayed liquids. Since acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.6.1 Place about 9.8 mL of reagent water into a 10-mL ground glass stoppered volumetric flask. For acrolein standards the reagent water must be adjusted to pH 4 to 5. Weight the flask to the nearest 0.1 mg.

6.6.2 Using a 100- μ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the water without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μ g/ μ L from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Optionally, stock standard solutions may be prepared using the pure standard material by volumetrically measuring the appropriate amounts and determining the weight of the material using the density of the material. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4 °C and protect from light.

6.6.5 Prepare fresh standards daily.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in reagent water that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary dilution standards should be prepared daily and stored at 4 °C.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1. Calibrate the purge

and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μ L of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25- μ L syringe with a 0.006 in. ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration of the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.4 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.6 and 6.7. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μ g/mL of each internal standard compound. The addition of 10 μ L of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μ g/L.

7.4.3 Analyze each calibration standard according to Section 10, adding 10 μ L of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

Equation 1

where:

A_s =Response for the parameter to be measured.

A_{is} =Response for the internal standard.

C_{is} =Concentration of the internal standard.

C_s =Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.5 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of a QC check sample.

7.5.1 Prepare the QC check sample as described in Section 8.2.2.

7.5.2 Analyze the QC check sample according to Section 10.

7.5.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 2. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, a new calibration curve, calibration factor, or RF must be prepared for that parameter according to Section 7.3 or 7.4.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1) to improve the separations or lower the cost of measurements. Each time such a

modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 25 µg/mL in reagent water. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 50 µg/L of each parameter by adding 200 µL of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to Section 10.

8.2.4 Calculate the average recovery (\bar{X}) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and \bar{X} with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and \bar{X} for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either s exceeds the precision limit or \bar{X} falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the

problem and repeat the test for each compound of interest.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 50 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to

contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P̄) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl₂) to the empty sample bottle just prior to shipping to the sampling site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁸ Field test kits are available for this purpose.

9.2 If acrolein is to be analyzed, collect about 500 mL of sample in a clean glass container. Adjust the pH of the sample to 4 to 5 using acid or base, measuring with narrow

range pH paper. Samples for acrolein analysis receiving no pH adjustment must be analyzed within 3 days of sampling.

9.3 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

9.4 All samples must be analyzed within 14 days of collection.³

10. Procedure

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and MDL that can be achieved under these conditions. An example of the separations achieved by Column 1 is shown in Figure 5. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 20 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.4 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 µL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 15.0 ± 0.1 min while heating at 85 ± 2 °C.

10.7 After the 15-min purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for 1.5 min.

10.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for 1.5 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 210 °C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.10 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

Equation 2

where:

A_s=Response for the parameter to be measured.

A_{is}=Response for the internal standard.

C_{is}=Concentration of the internal standard.

11.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above

zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.⁹ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method is recommended for the concentration range from the MDL to 1,000×MDL. Direct aqueous injection techniques should be used to measure concentration levels above 1,000×MDL.

12.3 In a single laboratory (Battelle-Columbus), the average recoveries and standard deviations presented in Table 2 were obtained.⁹ Seven replicate samples were analyzed at each spike level.

References

1. 40 CFR part 136, appendix B.
2. Bellar, T.A., and Lichtenberg, J.J. "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," *Journal American Water Works Association*, 66, 739 (1974).
3. "Evaluate Test Procedures for Acrolein and Acrylonitrile," Special letter report for EPA Project 4719-A, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, 27 June 1979.
4. "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
5. "OSHA Safety and Health Standards, General Industry," (29 CFR part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983).

8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

9. "Evaluation of Method 603 (Modified)," EPA-600/4-84-ABC, National Technical Information Service, PB84-, Springfield, Virginia 22161, Nov. 1984.

TABLE 1—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

| Parameter | Retention time (min) | | Method detection limit (µg/L) |
|---------------------|----------------------|----------|-------------------------------|
| | Column 1 | Column 2 | |
| Acrolein | 10.6 | 8.2 | 0.7 |
| Acrylonitrile | 12.7 | 9.8 | 0.5 |

Column 1 conditions: Porapak-QS (80/100 mesh) packed in a 10 ft × 2 mm ID glass or stainless steel column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 110 °C for 1.5 min (during desorption), then heated as rapidly as possible to 150 °C and held for 20 min; column bakeout at 190 °C for 10 min.⁹

Column 2 conditions: Chromosorb 101 (60/80 mesh) packed in a 6 ft. × 0.1 in. ID glass or stainless steel column with helium carrier gas at 40 mL/min flow rate. Column temperature held isothermal at 80 °C for 4 min, then programmed at 50 °C/min to 120 °C and held for 12 min.

TABLE 2—SINGLE LABORATORY ACCURACY AND PRECISION—METHOD 603

| Parameter | Sample matrix | Spike conc. (µg/L) | Average recovery (µg/L) | Standard deviation (µg/L) | Average percent recovery |
|---------------------|---------------|--------------------|-------------------------|---------------------------|--------------------------|
| Acrolein | RW | 5.0 | 5.2 | 0.2 | 104 |
| | RW | 50.0 | 51.4 | 0.7 | 103 |
| | POTW | 5.0 | 4.0 | 0.2 | 80 |
| | POTW | 50.0 | 44.4 | 0.8 | 89 |
| | IW | 5.0 | 0.1 | 0.1 | 2 |
| | IW | 100.0 | 9.3 | 1.1 | 9 |
| Acrylonitrile | RW | 5.0 | 4.2 | 0.2 | 84 |
| | RW | 50.0 | 51.4 | 1.5 | 103 |
| | POTW | 20.0 | 20.1 | 0.8 | 100 |
| | POTW | 100.0 | 101.3 | 1.5 | 101 |
| | IW | 10.0 | 9.1 | 0.8 | 91 |
| | IW | 100.0 | 104.0 | 3.2 | 104 |

ARW=Reagent water.

APOTW=Prechlorination secondary effluent from a municipal sewage treatment plant.

AIW=Industrial wastewater containing an unidentified acrolein reactant.

TABLE 3—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 603^A

| Parameter | Range for Q (µg/L) | Limit for S (µg/L) | Range for X (µg/L) | Range for P, P _s (%) |
|----------------|--------------------|--------------------|--------------------|---------------------------------|
| Acrolein | 45.9–54.1 | 4.6 | 42.9–60.1 | 88–118 |

TABLE 3—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 603^A—Continued

| Parameter | Range for Q ($\mu\text{g/L}$) | Limit for S ($\mu\text{g/L}$) | Range for X ($\mu\text{g/L}$) | Range for P, P _s (%) |
|---------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Acrylonitrile | 41.2–58.8 | 9.9 | 33.1–69.9 | 71–135 |

^A=Criteria were calculated assuming a QC check sample concentration of 50 $\mu\text{g/L}$.⁹

Q=Concentration measured in QC check sample, in $\mu\text{g/L}$ (Section 7.5.3).

s=Standard deviation of four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

X=Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

P, P_s=Percent recovery measured (Section 8.3.2, Section 8.4.2).

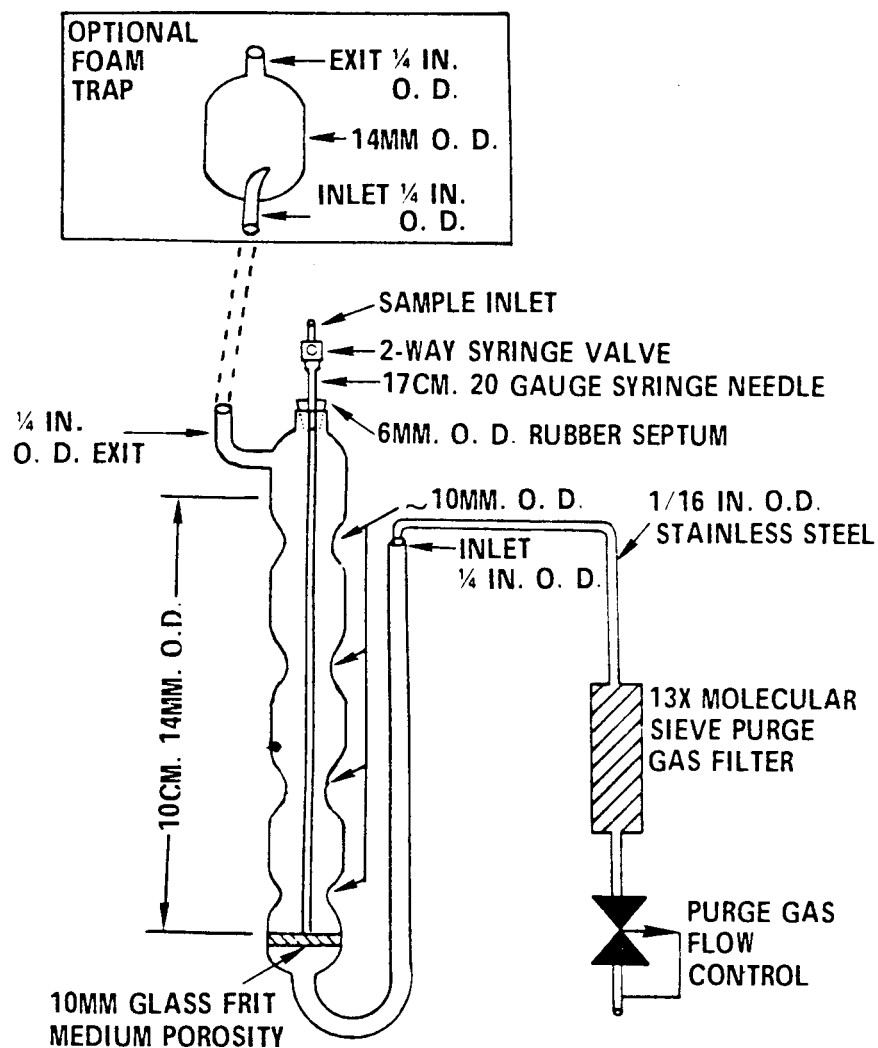


Figure 1. Purging device.

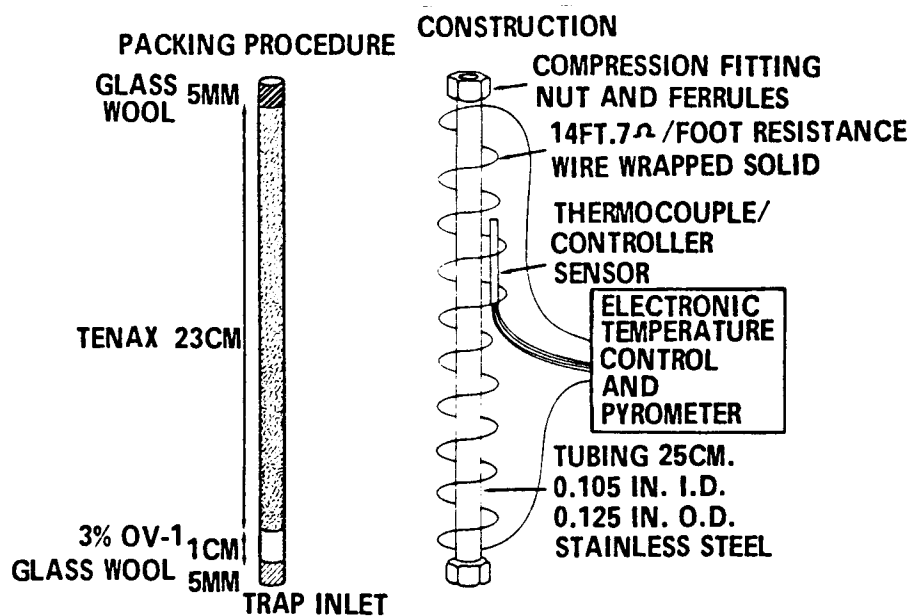


Figure 2. Trap packings and construction to include desorb capability.

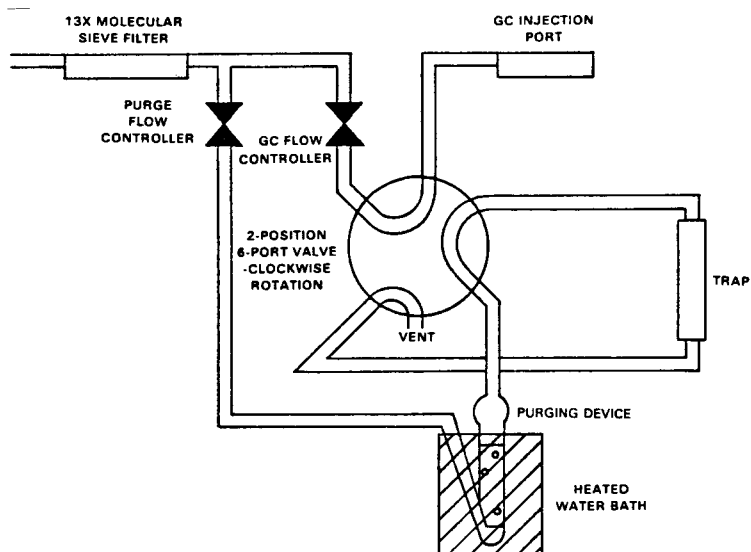


Figure 3. Purge and trap system-purge mode.

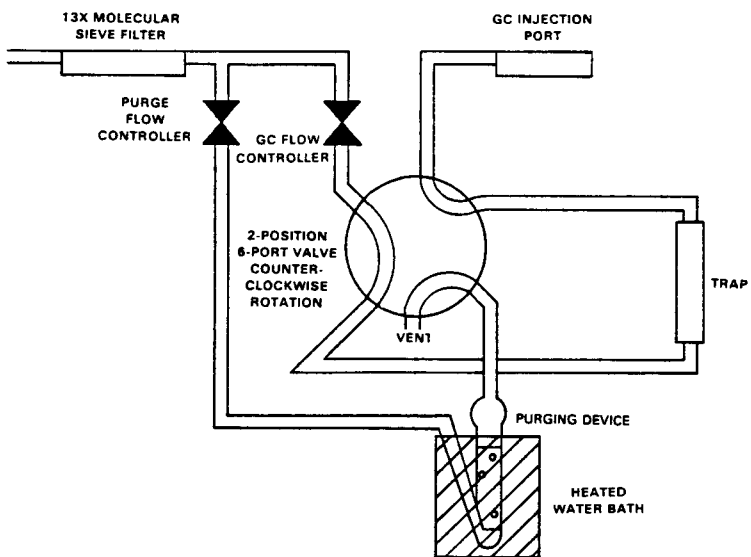


Figure 4. Purge and trap system-desorb mode.

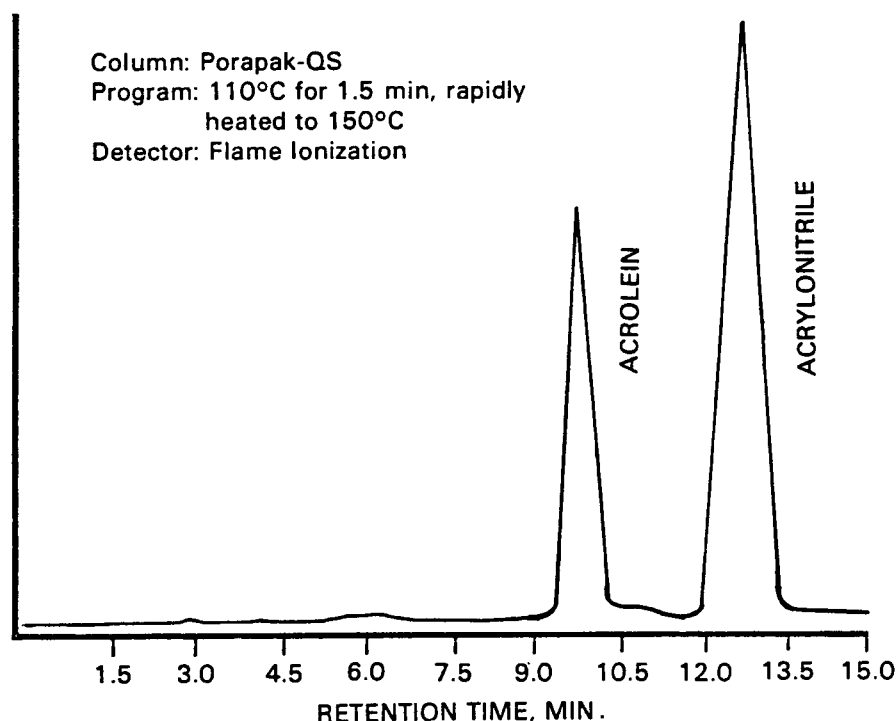


Figure 5. Gas chromatogram of acrolein and acrylonitrile.

METHOD 604—PHENOLS

1. Scope and Application

1.1 This method covers the determination of phenol and certain substituted phenols. The following parameters may be determined by this method:

| Parameter | STORET No. | CAS No. |
|----------------------------------|------------|----------|
| 4-Chloro-3-methylphenol | 34452 | 59-50-7 |
| 2-Chlorophenol | 34586 | 95-57-8 |
| 2,4-Dichlorophenol | 34601 | 120-83-2 |
| 2,4-Dimethylphenol | 34606 | 105-67-9 |
| 2,4-Dinitrophenol | 34616 | 51-28-5 |
| 2-Methyl-4,6-dinitrophenol | 34657 | 534-52-1 |
| 2-Nitrophenol | 34591 | 88-75-5 |
| 4-Nitrophenol | 34646 | 100-02-7 |
| Pentachlorophenol | 39032 | 87-86-5 |
| Phenol | 34694 | 108-95-2 |
| 2,4,6-Trichlorophenol | 34621 | 88-06-2 |

1.2 This is a flame ionization detector gas chromatographic (FIDGC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this

method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for derivatization, cleanup, and electron capture detector gas chromatography (ECDGC) that can be used to confirm measurements made by FIDGC. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix. The MDL listed in Table 1 for each parameter was achieved with a flame ionization detector (FID). The MDLs that were achieved when the derivatization cleanup and electron capture detector (ECD) were employed are presented in Table 2.